A new stable C_{NHC}^CH^C_{NHC} *N*-heterocyclic dicarbene ligand: its mono- and dinuclear Ir(I) and Ir(I)–Rh(I) complexes†

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The ligand [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazol-2-ylidene) (**2**) (abbreviated as $^{Et}C_{NHC}$^CH^C_{NHC} with CH = central aromatic ring, ^ = CH_2 spacer) has been synthesised, and isolated, by deprotonation of [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazolium) dichloride, $^{Et}(CH_{imid.}$^CH^$CH_{imid.})Cl_2$ (**1**) with $LiN(SiMe_3)_2$. This new, remarkably stable NHC dicarbene ligand is quantitatively protonated with HBr to form [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazolium) dibromide $^{Et}(CH_{imid.}$^CH^$CH_{imid.})Br_2$ (**3**) and reprotonated slowly enough in MeOH to allow observation of the monoprotonated intermediate **4**. Dicarbene **2** reacts with S_8 to give the dithione compound [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazol-2-thione) ^{Et}[(S=C)^CH^(C=S)] (**6**). Reaction of **2** with $[IrCl(CO)(PPh_3)_2]$ and $[Ir(\mu\text{-}Cl)(cod)]_2$ yielded the mononuclear $[Ir(CO)(PPh_3)_2$-$^{Et}(CH_{imid.}$^CH^$C_{NHC})(PF_6)](PF_6)$ (**8**) and $[IrCl(cod)^{Et}(CH_{imid.}$^CH^$C_{NHC})](PF_6)$ (**10**) complexes, respectively, and the dinuclear complexes $[\{Ir(CO)(PPh_3)_2\}_2{}^{Et}(\mu\text{-}C_{NHC}$^CH^$C_{NHC})](PF_6)_2$ (**7**) and $[\{IrCl(cod)\}_2{}^{Et}(\mu\text{-}C_{NHC}$^CH^$C_{NHC})]$ (**9**), respectively, in which **2** acts as a bridging, non-pincer type ligand. Only one other Ir(I) complex has been reported before containing a C_{NHC}^CH^C_{NHC} ligand. The structures of **6** and **9** were determined by X-ray diffraction and depict different conformations of the (1,3-phenylene)bis(methylene) (or xylylene) moiety. The mononuclear Ir complex **9** reacted smoothly with $[Rh(\mu\text{-}Cl)(cod)]_2$ and Cs_2CO_3 to generate a rare example of a heteronuclear NHC complex, $[IrRhCl_2(cod)_2{}^{Et}(\mu\text{-}C_{NHC}$^CH^$C_{NHC})]$ (**11**).

Introduction

In the course of the last fifteen years, *N*-heterocyclic carbene (NHC) ligands have emerged as a unique class of ligands, and their transition metal complexes have recently found impressive applications in homogeneous catalysis.[1–6] The isolation of 1,3-di-1-adamantyl-imidazol-2-ylidene by Arduengo *et al.*[7] in 1991 was key to this success since free carbenes ceased to be only regarded as highly reactive or fleeting intermediates. The kinetic stability of a free carbene appears to be governed by both electronic and steric parameters but remains rather difficult to anticipate. For example, bulky groups on nitrogen are no prerequisite for getting a "bottle-able" free carbene and *e.g.* tetramethyl-imidazol-2-ylidene is stable at room temperature under N_2.[8] The experimental conditions used to generate isolable free carbenes are also critical: the deprotonation of imidazolium salts (in this case the use of NaH in NH_3–THF or NH_3–CH_3CN mixture proved ingenious)[9,10] or the reduction of thione compounds[11,12] are both suitable routes. Dicarbene metal complexes are usually generated *in situ* by metallation of their imidazolium precursor.[4] The drawback of this method is that undesired reactions may occur between unreacted base and the metal precursors or the products.[13] Only few free dicarbenes have been isolated[12,14–19] and they often require storage temperatures below –15 °C (Scheme 1). In particular, $C_{NHC}CHC_{NHC}$ or $C_{NHC}NC_{NHC}$ dicarbene ligands have been isolated (**II**, **III**, **IV** and **V**, Scheme 1) and their reactivity, mostly in the case of $C_{NHC}NC_{NHC}$ ligands, has been investigated towards organic reagents[20] and transition metals.[18,19,21] However, the dicarbene ligands containing a methylene spacer, C_{NHC}^CH^C_{NHC} and C_{NHC}^N^C_{NHC}, have not been isolated but generated[10] and/or used *in situ* for the preparation of Ag,[22–27] Au,[28] Cu,[29] Pd,[23–25,27,30–36] rare-earth,[37] Ir[38] and Rh[24] complexes, and remain less studied than the $C_{NHC}CHC_{NHC}$ and $C_{NHC}NC_{NHC}$ systems.[21]

Although Ag(I),[22] Au(I),[28] Cu(II)[29] (non-pincer type), Pd(II),[25,30,31,35,36] or rare-earth elements[37] (pincer and non-pincer type) complexes have been prepared from the well-known salts $^{R}(CH_{imid.}$^CH^$CH_{imid.})X_2$ containing an imidazolium or a benzimidazolium core, only one Ir(I) complex has been reported, $[Ir(cod)^{i\text{-}Pr}(C_{NHC}$^CH^$C_{NHC})]Cl$ (triazolium core),[38a] before our work.[38b,c] Its structure was suggested to contain a chelating, non-pincer type dicarbene ligand.[38a] In view of potential catalytic applications, we were interested in isolating the new, potentially pincer dicarbene ligand $^{Et}C_{NHC}$^CH^C_{NHC} (^ is a CH_2 spacer) **2** in order to study its reactivity and coordination behaviour towards iridium complexes.

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† Electronic supplementary information (ESI) available: The formula of ligands and complexes described in this paper, the NMR spectra of compounds **1–11** and the CIF files for compounds **6** and **9**. CCDC reference numbers 706832 and 719957. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b902733e

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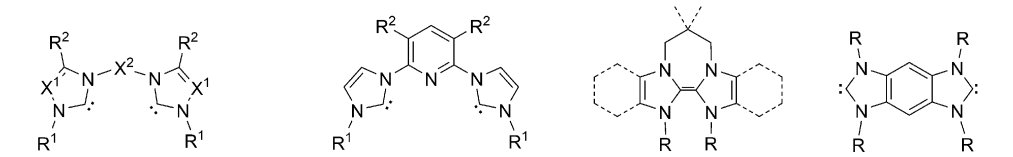
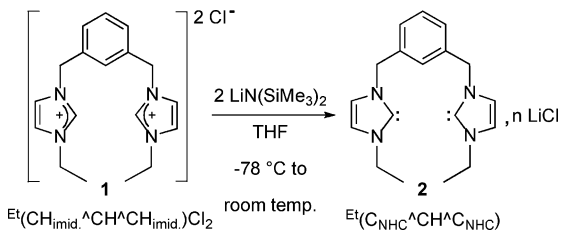


I R^1 = *t*-Bu; R^2 = H; X^1 = CH; X^2 = $(CH_2)_n$ (n = 1 or 2)
II R^1 = Ad; R^2 = Ph; X^1 = N; X^2 = 1,3-C_6H_4 or 1,4-C_6H_4
III R^1 = 2,6-*i*-$Pr_2C_6H_3$; R^2 = H
IV R^1 = (4-*t*-Bu-2,6-Me_2)C_6H_2; R^2 = H
V R^1 = 2,6-*i*-$Pr_2C_6H_3$; R^2 = CH_3
VI[a]
VII R = Ad, *t*-Bu, *t*-Amyl

Scheme 1 Isolated dicarbene ligands. *The dimer is in equilibrium with the free dicarbene in solution.[12,14,39]

Results and discussion

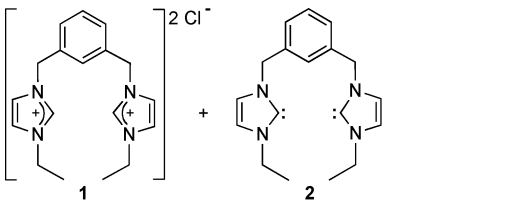
The salt [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazolium) dichloride $^{Et}(CH_{imid.}\text{^}CH\text{^}CH_{imid.})Cl_2$ (**1**) was prepared similarly to its methyl analog $^{Me}(CH_{imid.}\text{^}CH\text{^}CH_{imid.})Cl_2$,[40] but in contrast to the reactions of the latter with KO*t*-Bu or KH,[22] **1** was cleanly deprotonated by two equivalents of $LiN(SiMe_3)_2$ (THF, −78 °C) to yield the dicarbene ligand $^{Et}C_{NHC}\text{^}CH\text{^}C_{NHC}$ (**2**) (eqn (1), in general, the drawings do not intend to give an exact view of the molecular conformations).



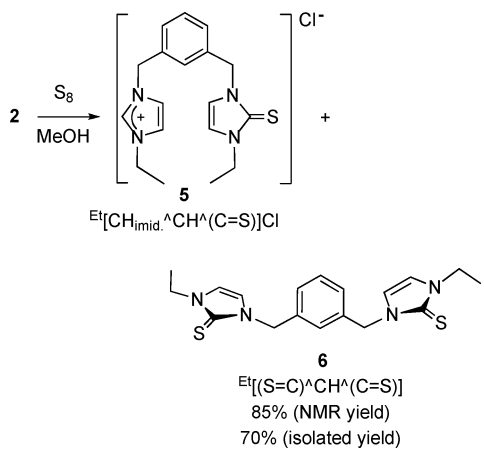
(1)

Compound **2** was collected as a white solid at the end of the reaction and could be stored under nitrogen at room temperature for months without any sign of decomposition. It is scarcely soluble in THF and aromatic solvents but soluble in more polar solvents such as DMSO and MeOH. Its ^1H NMR spectrum in d_6-DMSO confirmed the deprotonation of **1** since the resonance of the acidic NCHN proton at δ 9.82 ppm has disappeared and the other signals were upfield shifted by 0.1 (for CH_3) to 0.6 (for the aromatic protons) ppm. Progressive degradation of **2** in DMSO (the solution turns red after 0.5 h) and its reprotonation in alcohols (see below) prevented determination of the $^{13}C\{^1H\}$ NMR chemical shift of the carbene carbon. Although reprotonation of **2** with HBr instantly gave $^{Et}(CH_{imid.}\text{^}CH\text{^}CH_{imid.})Br_2$ (**3**) as indicated by the appearance of the ^1H NMR resonance for the NCHN protons at 9.48 ppm, reprotonation in MeOH was surprisingly slow enough to allow observation of a monoprotonated intermediate $[^{Et}CH_{imid.}\text{^}CH\text{^}C_{NHC}]OMe$ (**4**), which is suggested to have the proton bridging between the two carbenes (eqn (2), see ESI†).[41]

Formation of the dicarbene **2** was further demonstrated by its rapid reaction with S_8 which afforded the mono- and dithione derivatives $^{Et}[CH_{imid.}\text{^}CH\text{^}(C{=}S)]Cl$ (**5**) and $^{Et}[(S{=}C)\text{^}CH\text{^}(C{=}S)]$ (**6**), in 10–15% and 85% yield, respectively (eqn (3)). The presence of the chloride counterion in **5** suggests that it was already present in **2**, probably in the form of a LiCl adduct. Coordination of free carbene to soluble lithium salts is commonly observed and could explain the unexpected stability of the "deprotonated product".[42,43] Although this reaction was carried out in MeOH, neither formation of **1** or **4** was observed, consistent with



(2)



(3)

protonation of **2** being slower than thione formation. Compound **6** could also be obtained quantitatively from **1** or **5** by reacting them with Cs_2CO_3 and S_8 in MeOH at room temperature.

Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of pentane in a saturated dichloromethane solution of **6** (Fig. 1, Table 1).† The unit cell contains two crystallographically independent molecules A and B. For both molecules, the two imidazole rings are almost orthogonal to the central phenyl, and the C=S moieties are placed in the same half space defined by the aromatic ring (as represented in eqn (3)). The C=S distances (molecule A: C1–S1 = 1.694(2), C14–S2 = 1.678(2) Å; molecule B: C1–S1 = 1.686(2), C14–S2 = 1.682(2) Å) are in the range of values reported for mono-[44–46], di-[47–49] and trithione[50] compounds. The C1–N1, C1–N2, C14–N3 and C14–N4 distances in **6** are longer by nearly 0.05 Å than the corresponding distances

Table 1 Crystal data and structure refinement for **6** and **9**

	6	**9**
Chemical formula	$C_{18}H_{22}N_4S_2$	$C_{34}H_{46}Cl_2Ir_2N_4$
M_r	358.52	966.05
Cell setting, space group	Monoclinic, $P2_1/c$	Triclinic, P-1
Temperature/K	173(2)	173(2)
a/Å	14.1399(3)	10.5520(8)
b/Å	9.5935(3)	11.0660(8)
c/Å	28.2325(8)	15.0870(12)
α/°	90.00	101.543(5)
β/°	103.675(2)	98.061(4)
γ/°	90.00	101.036(3)
V/Å^3	3721.21(18)	1664.7(2)
Z	8	2
D_x/Mg m^{-3}	1.280	1.927
Radiation type	Mo Kα	Mo Kα
μ/mm^{-1}	0.29	8.18
Crystal form, colour	Prism, colourless	Cube, yellow
Crystal size/mm	$0.25 \times 0.15 \times 0.15$	$0.1 \times 0.1 \times 0.1$
Diffractometer	Kappa CCD	Kappa CCD
Data collection method	CCD	CCD
Absorption correction	None	Multi-scan (based on symmetry-related measurements)
T_{min}, T_{max}	—	0.410, 0.482
No. of measured, independent and observed reflections	13019, 8071, 5472	19970, 8774, 6327
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.027	0.068
θ_{max}/°	27.0	29.0
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, w$R(F^2)$, S	0.047, 0.150, 1.06	0.045, 0.106, 1.02
No. of reflections	8071	8774
No. of parameters	437	381
H-atom treatment	Constrained to parent site	Constrained to parent site
Weighting scheme	Calculated w = $1/[\sigma^2(F_o^2) + (0.0853P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated w = $1/[\sigma^2(F_o^2) + (0.0437P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.002	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.52, –0.32	3.50, –2.41

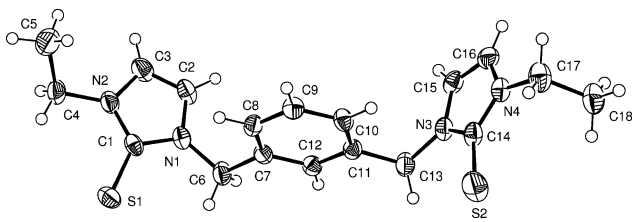
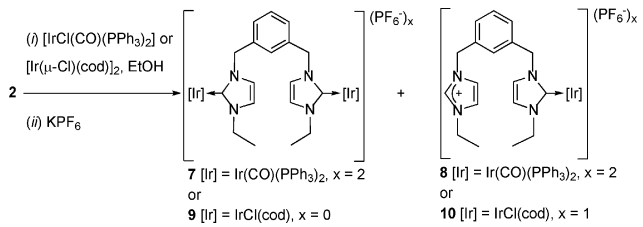


Fig. 1 ORTEP plot of the molecular structure of the dithione derivative ^{Et}[(S=C)^CH^(C=S)] (**6**). Ellipsoids are represented at 50% level probability level. Only one of the two crystallographically independent molecules is depicted (molecule A). Selected bonds distances (Å) and angles (°): Molecule A: C1–S1 1.694(2), C1–N1 1.357(2), C1–N2 1.360(3), C14–S2 1.678(2), C14–N3 1.365(3), C14–N4 1.354(3), N1–C1–S1 126.8(2), N2–C1–S1 127.6(2), N3–C14–S2 127.3(2), N4–C14–S2 127.3(2); Molecule B: C1–S1 1.686(2), C1–N1 1.363(3), C1–N2 1.358(3), C14–S2 1.682(2), C14–N3 1.362(3), C14–N4 1.360(3), N1–C1–S1 127.3(2), N2–C1–S1 127.4(2), N3–C14–S2 126.8(2), N4–C14–S2 128.3(2).

in the parent imidazolium salt,[40] which parallels the decreased π delocalization in the dithione compound.[4]

The molecular structure indicated a C_1 symmetry for **6** in the solid state, but only one set of NMR signals was observed, in agreement with an average C_2 symmetry of the molecule in solution. The $^{13}C\{^1H\}$ NMR signal at 161.2 ppm for **6** is characteristic of the C2 thione carbon.[4]

Although the reaction of **2** with Vaska's complex in ethanol at room temperature may have been anticipated to afford a mononuclear, chelate complex, it afforded a mixture of $[\{Ir(CO)(PPh_3)_2\}_2{}^{Et}(\mu\text{-}C_{NHC}\text{^}CH\text{^}C_{NHC})](PF_6)_2$ (**7**) and $[Ir(CO)(PPh_3)_2{}^{Et}(CH_{imid.}\text{^}CH\text{^}C_{NHC})(PF_6)](PF_6)$ (**8**) in 24 and 18% isolated yield, respectively, in which the metal is bound to only one carbene function (eqn (4)).



(4)

Exchange of the chloride counterion with PF_6^- facilitated the separation of these cationic complexes by column chromatography. The $^{31}P\{^1H\}$ NMR spectrum of **7** contained a singlet at 21.0 ppm for the equivalent *trans* PPh_3 ligands and the ^1H NMR spectrum in CD_2Cl_2 showed a shielding of all the protons compared to **1** and the spacer CH_2 protons gave rise to a singlet at δ 4.30 ppm. The two equivalent carbene carbons gave rise to a triplet in $^{13}C\{^1H\}$ NMR at δ 174.1 ppm ($^2J(CP) = 13.7$ Hz), a value comparable to those for cationic NHC Ir(I) complexes.[51–54]

The presence of the CO ligands is confirmed by the ν(CO) vibration at 1991 cm^{-1} and by the triplet observed in the $^{13}C\{^1H\}$ NMR spectrum (δ 184.6 ppm). The ^1H NMR spectrum of **8** shows a strong shielding of the coordinated arm in contrast to the imidazolium "non-coordinated" arm of the molecule. The NCHN imidazolium proton gave a characteristic broad singlet at δ 8.66 ppm in the ^1H NMR spectrum and the carbene and carbonyl carbons showed $^{13}C\{^1H\}$ NMR signals almost identical to those of **7**. Displacement of a chloride anion instead of a neutral PPh_3 ligand in eqn (4) could result from facilitated chloride decoordination from the Ir(I) centre in a polar solvent.[55]

The reaction of **2** with $[Ir(\mu\text{-}Cl)(cod)]_2$ afforded similarly the dinuclear complex $[\{IrCl(cod)\}_2{}^{Et}(\mu\text{-}C_{NHC}\text{^}CH\text{^}C_{NHC})]$ (**9**) and the mono-NHC complex $[IrCl(cod)^{Et}(CH_{imid.}\text{^}CH\text{^}C_{NHC})](PF_6)$ (**10**) (eqn (4)). No pincer-type complex was observed under these conditions or even upon heating the reaction mixture in acetonitrile at 60 °C. The selective precipitation of **10** from CH_2Cl_2–Et_2O facilitated the separation of these two Ir(I) complexes. The molecular structure of **9**, determined by X-ray diffraction,† has no symmetry element (Fig. 2, Table 1) and the Ir(cod) fragments occupy positions that minimize steric repulsion.

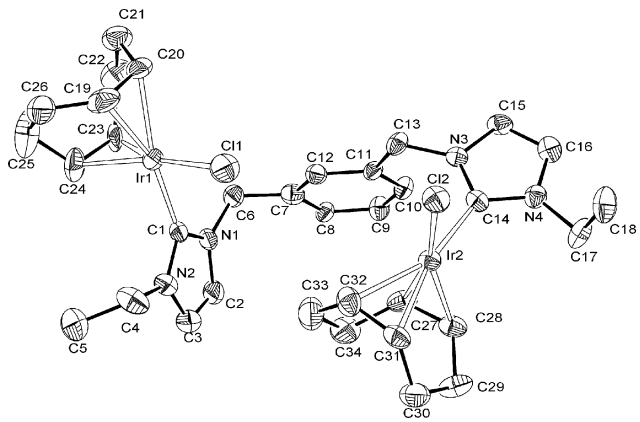
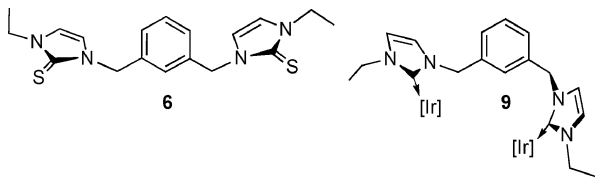


Fig. 2 ORTEP plot of the molecular structure of **9**. Hydrogen atoms omitted for clarity. Ellipsoids are represented at 50% level probability level. Selected bonds distances (Å) and angles (°): Ir1–C1 2.035(6), Ir1–C19 2.184(7), Ir1–C20 2.191(6), Ir1–C23 2.034(8), Ir1–C24 2.126(6), Ir2–C14 2.045(6), C27–C28 1.405(8), C31–C32 1.386(8); C1–Ir1–C19 158.0(3), C1–Ir1–C20 164.6(3), C1–Ir1–C23 91.2(3), C1–Ir1–C24 91.5(3), C1–Ir1–Cl1 90.3(2), C14–Ir2–Cl 2 89.7(2).

In $[\{RhCl(cod)\}_2{}^{n\text{-}Bu}(\mu\text{-}C_{NHC}\text{^}N\text{^}C_{NHC})]$,[24] the metal–metal separation (6.333(2) Å) is shorter that in **9** (7.0817(5) Å). Another important difference between these two structures concerns the orientation of the chloride ligands: in **9** the ligand Cl1 is directed towards the hydrogen atom H12 of the central aryl (2.944(2) Å) whereas Cl2 in $[\{RhCl(cod)\}_2{}^{n\text{-}Bu}(\mu\text{-}C_{NHC}\text{^}N\text{^}C_{NHC})]$ is further away from the central nitrogen atom (5.77(2) Å), probably to avoid electronic repulsion between their lone pairs. In **9**, the Ir1–C19 and Ir1–C20 distances are longer than Ir1–C23 and Ir1–C24, and C31–C32 is shorter than C27–C28, which reflects the larger *trans* influence of the carbene ligand compared to chloride. This is consistent with data on other NHC–Ir(I) complexes.[38,56,57]

A comparison of the crystal structures of **6** and **9** reveals a different orientation of the CH_2 spacer and of the imidazole rings (Scheme 2). The ^1H NMR spectrum of **9** contains two AB



Scheme 2 Differing conformations of the "xylylene" moiety in **6** and **9** based on their solid-state structure.

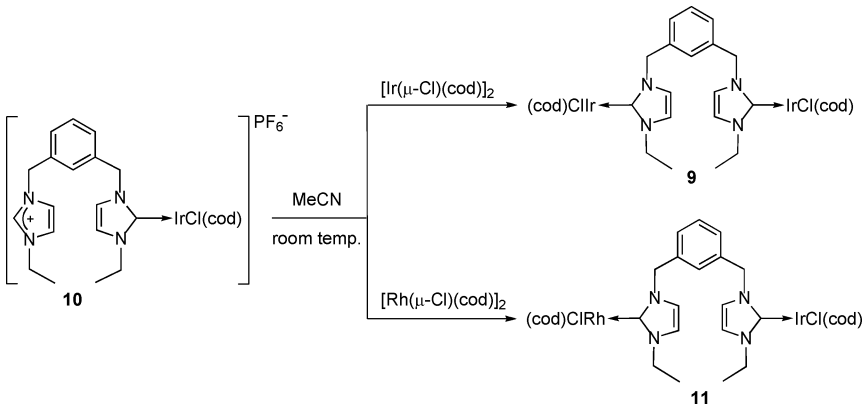
systems for the hydrogen atoms of the CH_2 spacers and the ^{13}C NMR spectrum contains two signals for the carbene carbon at δ 180.1 and 180.2 ppm. This could be explained by the presence in solution of a single diastereoisomer with a conformation similar to that observed in the solid-state or by the coexistence of two different diastereoisomers in a 1 : 1 ratio resulting from different orientations for the CH_2 spacers and the imidazole rings (see ESI†). On the basis of these X-ray structures, one could suggest that if the imidazole rings in **2** remain in solution far away from the C12–H12 bond, formation of pincer complexes will be disfavoured, as indeed observed.

As expected, the ^1H NMR spectrum of **10** in CD_2Cl_2 showed the characteristic NCHN proton resonance at 8.76 ppm. The CH_2 spacer hydrogen atoms gave rise to two doublets for the coordinated arm and to an AB spin system for the imidazolium "non-coordinated" arm of the molecule, which highlights a restricted rotation of the imidazole ring, probably due to the adjacent iridium moiety. HMBC analysis of **10** allows the differentiation between the two arms of the molecule. Other NMR signals, in particular the $^{13}C\text{-}\{^1H\}$ NMR resonance at δ 179.9 ppm for the carbene carbon, are in the range reported for other NHC–Ir(I) complexes.[38,53]

The reactivity of **10** towards bases was studied with the aim to metalate the second arm of the ligand. Whereas **10** did not react with Ag_2O in CH_2Cl_2, the use of *n*-BuLi led to decomposition of the complex. However, **10** reacted smoothly with one equivalent of the Ir(I) precursor in the presence of Cs_2CO_3 to form **9**, which emphasizes the critical importance of the choice of the base. Replacement of Ir(I) with Rh(I) led selectively (^1H NMR data, including ^1J(RhC) couplings, and mass spectrometry evidence) to the heterobimetallic complex **11** in 89% yield (Scheme 3).

In solution, **11** is present as a 1 : 1 mixture of two diastereoisomers, as indicated by the observation in the ^1H NMR spectrum of four AB spin systems for the spacer CH_2 protons and in $^{13}C\{^1H\}$ NMR by two distinct doublets for the rhodium-bound carbene carbons. This is consistent with the lack of symmetry element relating the two metal centres, which are now chemically different, in contrast to **9**. To the best of our knowledge, only two other heterodinuclear NHC complexes have been reported to date, also with the Ir–Rh couple.[58,59] Further reactivity studies are in progress.

In conclusion, we have isolated the new, stable dicarbene ligand **2**, and structurally characterised its dithione derivative. The dicarbene ligand readily forms dinuclear Ir(I) complexes and, in a stepwise manner, heterodinuclear Ir(I)–Rh(I) complexes. This stepwise method appears promising and could be used to prepare other types of heteronuclear systems. A "bottle-able" dicarbene ligand offers specific synthetic advantages when the *in situ* preparation of the metal complexes from the bis(imidazolium) carbene precursors affords lower yields or would fail. This approach also offers the advantage of avoiding the use of additional bases, required for



Scheme 3 Stepwise synthesis of homo- and heterodinuclear carbene complexes.

the *in situ* syntheses, which can be detrimental to the stability of the metal complexes. The fact that ligands such as **2** may act as bridges rather than chelates is important to keep in mind when attempting to prepare "pincer-type" complexes requiring a chelating behaviour of the ligand. It is suggested that conformation effects explain the lack of formation of pincer complexes with **2** and its unusual bridging behaviour.

Experimental

General procedures

All operations were carried out using standard Schlenk techniques under inert atmosphere. The synthesis of the imidazolium salts was conducted under nitrogen, whereas that of the complexes was performed under argon. Solvents were dried, degassed, and freshly distilled prior to use. THF and Et_2O were dried over sodium–benzophenone. The solvents CH_2Cl_2 and CH_3CN were distilled from CaH_2 and d_6-DMSO and CD_3CN were degassed and stored over 4 Å molecular sieves. CD_2Cl_2 was dried over 4 Å molecular sieves, degassed by freeze–pump–thaw cycles and stored under argon. NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer (^1H, 300 MHz; ^{13}C, 75.47 MHz) and referenced using the residual proton solvent (^1H) or solvent (^{13}C) resonance. Assignments are based on ^1H, ^1H-COSY, ^1H, ^{13}C-HMQC and ^1H, ^{13}C-HMBC experiments. IR spectra were recorded in the region 4000–100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the "Service de microanalyses", Université de Strasbourg and the "Service Central d'Analyses", USR-59/CNRS, Solaize. Electrospray Mass Spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulising gas and Maldi-TOF analyses were carried out on a Bruker AutiflexII TOF/TOF (Bruker Daltonics, Bremen, Germany), using dithranol (1,8,9-trihydroxyanthracene) as a matrix. Potassium imidazolide ($KC_3H_3N_2$) was obtained in quantitative yield by mixing imidazole and KO*t*-Bu in toluene and heating to 110 °C. 1-Ethylimidazole was prepared by reaction of potassium imidazolide with ethyl iodide in THF at room temperature and was isolated as a colourless oil in 70% yield after filtration, evaporation and distillation (bp 97–98 °C at 27 mmHg) of the reaction mixture (for analytical data, see ref. 60). All other reagents were used as received from commercial suppliers. Yields of the metal complexes are based on iridium. In the assignment of the spectroscopic data, the abbreviation "coord." corresponds to the values for the coordinated arm of the ligand when an imidazolium moiety remains non-coordinated.

Synthesis of [(1,3-phenylene)bis(methylene)]bis (1-ethyl-imidazolium) dichloride, $^{Et}(CH_{imid.}{\wedge}CH{\wedge}CH_{imid.})Cl_2$ (1)

The procedure published for [(1,3-phenylene)bis(methylene)]bis(1-methyl-imidazolium) dichloride, $^{Me}(CH_{imid.}{\wedge}CH{\wedge}CH_{imid.})Cl_2$,[40] was slightly modified as follows. A mixture of solid 1,3-bis (chloromethyl)benzene (8.790 g, 49.2 mmol) and pure 1-ethyl-imidazole (9.650 g, 100.4 mmol) was stirred and heated to 135 °C for 10 min. The solid obtained was then allowed to cool to room temperature, washed with THF (2 × 20 mL), which dissolves the reagents but not the product, yielding **1** as a hygroscopic colourless solid in 98% yield (17.71 g, 48.2 mmol). ^1H NMR (d_6-DMSO): δ 1.43 (t, $^3J(HH) = 7.3$ Hz, 6H, CH_3), 4.25 (q, $^3J(HH) = 7.3$ Hz, 4H, CH_3CH_2), 5.49 (s, 4H, CH_2), 7.45–7.50 (m, 3H, CH arom.), 7.76 (s, 1H, CH arom.), 7.89 (*pseudo* t, $^3J(HH) = {}^4J(HH) = 1.6$ Hz, 2H, CH imid.), 7.97 (*pseudo* t, $^3J(HH) = {}^4J(HH) = 1.6$ Hz, 2H, CH imid.), 9.82 (*pseudo* t, $^4J(HH) = 1.6$ Hz, 2H, NCHN). $^{13}C\{^1H\}$ NMR (d_6-DMSO): δ 15.0 (CH_3), 44.3 (CH_3CH_2), 51.4 (CH_2), 122.4 (CH imid.), 122.5 (CH imid.), 128.6 (CH arom.), 128.7 (CH arom.), 129.6 (CH arom.), 135.7 (C arom.), 136.2 (N*C*HN). ESI-MS (CH_3OH, 10 V, *m*/*z*): 331.2 $[M - Cl]^+$, 295.2 $[M - 2Cl - H]^+$. HRMS (ESI) $[M - Cl]^+$: 331.1712 calcd for $C_{18}H_{24}ClN_4$: 331.1684. Anal. Calc. for $C_{18}H_{24}Cl_2N_4$ (367.32): C, 58.86; H, 6.59; N, 15.25. Found: C, 57.69; H, 7.25; N, 14.68%. Despite several attempts, better elemental analyses could not be obtained owing to the strongly hygroscopic properties of this compound. IR (pure, diamond orbit): 3365 wbr, 3129 w, 3043 mbr, 2970 mbr, 2869 wbr, 1612 w, 1557 s, 1491 w, 1446 s, 1352 m, 1321 m, 1254 w, 1154 vs, 1093 m, 1021 m, 975 w, 955 w, 752 s, 729 vs cm^{-1}.

Synthesis of [(1,3-phenylene)bis(methylene)]bis (1-ethyl-imidazol-2-ylidene), $^{Et}C_{NHC}{\wedge}CH{\wedge}C_{NHC}$ (2)

Solid lithium bis(trimethylsilyl)amide (0.192 g, 1.26 mmol) and [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazolium) dichloride (**1**, 0.210 g, 0.57 mmol) were mixed and cooled to −78 °C and THF (10 mL) was added dropwise. The reaction mixture was

warmed to room temperature and stirred for 15 h. The solvent was then removed *in vacuo* and the crude product was washed with THF (6 mL) yielding 0.134 g of **2** as a white solid, which corresponds to 80% yield (0.46 mmol based on free NHC), 62% yield (0.35 mmol based on NHC·2LiCl) or 70% yield (0.40 mmol based on NHC·LiCl). ^{1}H NMR (d_6-DMSO): δ 1.34 (t, ^3J(HH) = 7.3 Hz, 6H, CH_3), 4.02 (q, ^3J(HH) = 7.3 Hz, 4H, CH_3CH_2), 5.20 (s, 4H, CH_2), 7.20–7.34 (m, 8H, 4 CH arom. and 4 CH imid.). Anal. Calc. for $C_{18}H_{22}N_4$·5LiCl: C, 42.70; H, 4.38; N, 11.06. Found: C, 45.72; H, 6.39; N, 10.92%. There is uncertainty about the amount of LiCl present in the sample, but the atomic C : N ratio found to be 4.88 is satisfactory. IR (pure, diamond orbit): 3053 br, 2974 br, 2866 wbr, 1612 w, 1554 s, 1449 m, 1353 w, 1257 w, 1240 w, 1159 vs, 1093 w, 1065 w, 1018 w, 955 w, 824 mbr, 756 sh, 733 vs cm^{-1}.

Synthesis of [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazolium) dibromide, ^{Et}(CH$_{imid.}$^CH^CH$_{imid.}$)Br$_2$ (3)

In a NMR tube two drops of pure HBr were added to a fresh solution of [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazol-2-ylidene) **2** (0.010 g, 0.034 mmol) in d_6-DMSO (0.25 mL). The tube was closed and shaken. NMR analysis of the colourless solution indicated quantitative formation of **3** (the signal at 5.89 ppm corresponds to excess HBr). ^{1}H NMR (d_6-DMSO): δ 1.34 (t, ^3J(HH) = 7.3 Hz, 6H, CH_3), 4.17 (q, ^3J(HH) = 7.3 Hz, 4H, CH_3CH_2), 5.42 (s, 4H, CH_2), 7.33–7.47 (m, 3H, CH arom.), 7.63 (s, 1H, CH arom.), 7.77 (*pseudo* t, ^3J(HH) = ^4J(HH) = 1.6 Hz, 2H, CH imid.), 7.80 (*pseudo* t, ^3J(HH) = ^4J(HH) = 1.6 Hz, 2H, CH imid.), 9.48 (br s, 2H, NCHN).

Observation of the monoprotonated compound [^{Et}CH$_{imid.}$^CH^C$_{NHC}$]OMe (4)

(a) From the reaction between 1 and 2 in d_6-DMSO. In a NMR tube, a solution of **2** (0.005 g, 0.017 mmol) in d_6-DMSO (0.10 mL) was added to a solution of **1** (0.006 g, 0.017 mmol) in d_6-DMSO (0.10 mL). The tube was closed and shaken. ^{1}H NMR analysis of the solution indicated quantitative formation of **4**. ^{1}H NMR (d_6-DMSO): δ 1.43 (t, ^3J(HH) = 7.3 Hz, 6H, CH_3), 4.23 (q, ^3J(HH) = 7.3 Hz, 4H, CH_3CH_2), 5.46 (s, 4H, CH_2), 7.45 (br s, 3H, CH arom.), 7.67 (br s, 1H, CH arom.), 7.84 and 7.88 (AB spin system, ^3J(HH) = 1.8 Hz, 4H, CH imid.), 8.70–10.70 (vbr s, 1H, NCHN). The solution became orange-red after 1 h, preventing determination of the ^{13}C NMR chemical shift of the NCN carbon atoms.

(b) From protonation of 2 in MeOH. Compound **2** (0.010 g, 0.034 mmol) was dissolved in MeOH and stirred for 15 h at room temperature. The solvent was then removed *in vacuo* and the crude product was analysed by ^{1}H NMR, which indicated the formation of **4**.

We suggest that the anion associated with the cationic part of **4** is MeO^-, although the presence of OH^- cannot be ruled out when water is present.

Even if these reactions demonstrated that **2** is reprotonated in MeOH (and alcohols in general), the limited solubility of **2** in other organic solvents limited the study of its reactivity in these solvents.

Observation of [(1,3-phenylene)bis(methylene)]-(1-ethyl-imidazolium)-(3-ethyl-imidazol-2-thione) chloride, ^{Et}[CH$_{imid.}$^CH^(C=S)]Cl (5)

This compound was observed in the crude product during the synthesis of [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazol-2-thione) **6** but was not isolated pure. Selected data assigned to **5**: ^{1}H NMR (d_6-DMSO): δ 1.23 (t, ^3J(HH) = 7.2 Hz, 3H, CH_3), 1.43 (t, ^3J(HH) = 7.3 Hz, 3H, CH_3 imidazolium), 3.98 (q, ^3J(HH) = 7.2 Hz, 2H, CH_3CH_2 partly masked by signals of **6**), 4.22 (q, ^3J(HH) = 7.3 Hz, 2H, CH_3CH_2 imidazolium), 5.20 (s, 2H, CH_2), 5.45 (s, 2H, CH_2 imidazolium), 7.13–7.18 (m, 4H, 2 CH arom. and 2 CH imid. partly masked by signals of **6**), 7.32–7.50 (m, 2H, CH arom. partly masked by signals of **6**), 7.90 (*pseudo* t, ^3J(HH) = ^4J(HH) = 1.6 Hz, 1H, CH imidazolium), 7.92 (*pseudo* t, ^3J(HH) = ^4J(HH) = 1.6 Hz, 1H, CH imidazolium), 9.76 (*pseudo* t, ^4J(HH) = 1.6 Hz, 1H, NCHN). ESI-MS (CH_3OH, 10 V, *m*/*z*): 327.2 [M – Cl]$^+$.

Synthesis of [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazol-2-thione), ^{Et}[(S=C)^CH^(C=S)] (6)

(a) From 2. A solution of [(1,3-phenylene)bis(methylene)] bis(1-ethyl-imidazol-2-ylidene) **2** (0.844 g, 2.21 mmol) in MeOH (10 mL) was quickly added to a suspension of flowers of sulfur (0.142 g, 4.42 mmol) in MeOH (40 mL) and the mixture was stirred at room temperature for 12 h. The solvent was then removed *in vacuo* and the crude product was purified by chromatography on silica gel with MeOH as eluant. The orange solid obtained after removal of the solvent *in vacuo* was triturated with water (2 × 10 mL) and dried under vacuum overnight. Recrystallisation from dichloromethane–pentane gave **6** as a white solid in 70% yield (0.555 g, 1.55 mmol). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated dichloromethane solution of **6**. ^{1}H NMR (d_6-DMSO): δ 1.24 (t, ^3J(HH) = 7.2 Hz, 6H, CH_3), 3.98 (q, ^3J(HH) = 7.2 Hz, 4H, CH_3CH_2), 5.18 (s, 4H, CH_2), 7.13 and 7.19 (AB spin system, ^3J(HH) = 2.4 Hz, 4H, CH imid.), 7.14–7.18 (m, 2H, CH arom.), 7.26–7.32 (m, 2H, CH arom.). ^{13}C{^{1}H} NMR (d_6-DMSO): δ 14.1 (CH_3), 42.1 (CH_3CH_2), 49.5 (CH_2), 117.2 (CH imid.), 117.4 (CH imid.), 126.8 (CH arom.), 127.1 (CH arom.), 128.7 (CH arom.), 137.3 (C arom.), 161.2 (N(*C*=S)N). ESI-MS (CH_3OH, 43 V, *m*/*z*): 397.1 [M + K]$^+$, 381.1 [M + Na]$^+$, 365.1 [M + Li]$^+$, 359.1 [M + H]$^+$. Anal. Calc. for $C_{18}H_{22}N_4S_2$ (358.52): C, 60.30; H, 6.18; N, 15.63. Found: C, 60.13; H, 6.47; N, 15.87%. IR (pure, diamond orbit): 3150 w, 3121 w, 3092 w, 2921 wbr, 2849 w, 1440 m, 1409 s, 1306 m, 1267 s, 1235 vs, 1193 s, 1137 sbr, 983 m, 802 w, 770 m, 754 m, 722 m, 678 m cm^{-1}.

(b) From 1 and/or 5. Compounds **1** and **5** could be converted almost quantitatively in **6** by reaction with Cs_2CO_3 and S_8 in MeOH at room temperature for 15 h. The resulting suspension was filtered and the solvent was then removed *in vacuo*. The orange solid obtained was triturated with water and dried under vacuum for overnight. Recrystallisation from dichloromethane–pentane gave **6** as a white solid.

Synthesis of [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazol-2-ylidene)-bis[*trans*-carbonylbis(triphenylphosphine)iridium(I)] dihexafluorophosphate, [{Ir(CO)(PPh$_3$)$_2$}$_2$^{Et}(μ-C$_{NHC}$^CH^C$_{NHC}$)](PF$_6$)$_2$ (7)

A solution of compound **2** (0.300 g, 0.72 mmol) in ethanol (15 mL) was rapidly added to a suspension of *trans*-[IrCl(CO)(PPh$_3$)$_2$] (0.516 g, 0.66 mmol) in ethanol (20 mL). The reaction mixture was stirred at room temperature for 15 h and the solvent was removed *in vacuo*. The crude product was dissolved in dichloromethane (5 mL), the solution was filtered and washed with deionised water saturated with KPF_6 (10 mL). The organic layer was then washed with deionised water (3 × 10 mL), collected, dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The crude product was purified by chromatography on silica gel (dichloromethane : acetone 9 : 1 and KPF_6) yielding **7** as a yellow solid. Elution with a more polar solvent mixture (dichloromethane : acetone 7 : 3 and KPF_6) yielded **8** (see below). Solubilisation of the complex in dichloromethane followed by filtration allows the elimination of excess KPF_6. Recrystallisation from CH_2Cl_2–pentane yielded pure **7** in 24% yield (0.165 g, 0.08 mmol). ^{1}H NMR (CD_2Cl_2): δ 0.54 (t, ^3J(HH) = 7.4 Hz, 6H, CH_3), 3.22 (q, ^3J(HH) = 7.4 Hz, 4H, CH_2CH$_3$), 4.30 (s, 4H, CH_2), 6.06 (br d, ^3J(HH) = 7.7 Hz, 2H, C*H*–CH–C*H* xylene), 6.28 (br s, 1H, C–CH–C xylene), 6.33 (t, ^3J(HH) = 7.7 Hz, 1H, CH–C*H*–CH xylene), 6.53 (d, ^3J(HH) = 1.5 Hz, 2H, CH imid.), 6.78 (d, ^3J(HH) = 1.5 Hz, 2H, CH imid.), 7.37–7.58 (m, 60H, PPh_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 13.8 (CH_3), 46.1 (CH$_3$*C*H$_2$), 54.6 (*C*H$_2$), 122.3 (CH imid.), 122.8 (CH imid.), 129.6 (virtual t, ^{3+5}J(CP) = 10.0 Hz, *meta*-C PPh_3), 130.0 (CH arom.), 130.2 (CH arom.), 130.8 (CH arom.), 132.0 (s, *para*-C PPh_3), 132.2 (virtual t, ^{1+3}J(CP) = 54.4 Hz, *ipso*-C PPh_3), 134.3 (virtual t, ^{2+4}J(CP) = 12.2 Hz, *ortho*-C PPh_3), 134.6 (C arom.), 174.1 (t, ^2J(CP) = 13.7 Hz, C–Ir), 184.6 (t, ^2J(CP) = 11.7 Hz, CO). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −73.4 (d, ^1J(FP) = 711.3 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −143.2 (sept, ^1J(PF) = 711.3 Hz, PF_6), 21.0 (s, PPh_3). MALDI TOF-MS (CH_3CN, *m*/*z*): 1927.3 [M − PF_6]$^+$. Anal. Calc. for $C_{92}H_{82}F_{12}Ir_2N_4P_6O_2$ (2073.92): C, 53.28; H, 3.99; N, 2.70. Found: C, 53.00; H, 4.25; N, 2.47%. IR (pure, diamond orbit): 3178 w, 3136 w, 3054 wbr, 2946 w, 1983 s (ν_{CO}), 1570 w, 1480 m, 1434 m, 1310 w, 1260 w, 1220 w, 1184 w, 1094 m, 1027 w, 999 w, 831 vs, 742 s, 691 vs, 556 s, 514 s, 496 s, 455 w, 418 m cm^{-1}.

Synthesis of [(1,3-phenylene)bis(methylene)]-(1-ethyl-imidazolium)-(3-ethyl-imidazol-2-ylidene)-hexafluorophosphate-[*trans*-carbonylbis(triphenylphosphine)iridium(I)] hexafluorophosphate, [IrCO(PPh$_3$)$_2$^{Et}(CH$_{imid.}$^CH^C$_{NHC}$)(PF$_6$)][PF$_6$) (8)

Compound **2** (0.300 g, 0.72 mmol) in ethanol (15 mL) was rapidly added to a suspension of *trans*-[IrCl(CO)(PPh$_3$)$_2$] (0.516 g, 0.66 mmol) in ethanol (20 mL). The reaction mixture was stirred at room temperature for 15 h and the solvent was removed *in vacuo*. The crude product was dissolved in dichloromethane (5 mL), the solution was filtered and washed with deionised water saturated with KPF_6 (10 mL). The organic layer was then washed with deionised water (3 × 10 mL), collected, dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The crude product was purified by chromatography on silica gel (dichloromethane : acetone 7 : 3 and KPF_6) to yield a yellow solid. Solubilisation of the complex in dichloromethane followed by filtration allows the elimination of excess KPF_6. Recrystallisation from dichloromethane–pentane yielded pure **8** in 18% yield (0.158 g, 0.12 mmol). ^{1}H NMR (CD_2Cl_2): δ 0.53 (t, ^3J(HH) = 7.4 Hz, 3H, coord. CH_3), 1.58 (t, ^3J(HH) = 7.4 Hz, 3H, CH_3), 3.23 (q, ^3J(HH) = 7.4 Hz, 2H, coord. CH_2CH$_3$), 4.26 (q, ^3J(HH) = 7.4 Hz, 2H, CH_2CH$_3$), 4.34 (s, 2H, coord. CH_2), 5.22 (s, 2H, CH_2), 6.34 (br d, ^3J(HH) = 7.7 Hz, 1H, C–C*H*–CH xylene), 6.67 and 6.75 (AB spin system, ^3J(HH) = 2.0 Hz, 2H, CH imid.), 6.90 (s, 1H, C–CH–C xylene), 6.94 (t, ^3J(HH) = 7.7 Hz, 1H, CH–C*H*–CH xylene), 7.23 (br d, ^3J(HH) = 7.7 Hz, 1H, C–C*H*–CH xylene), 7.29–7.59 (m, 32H, PPh_3 and 2 × CH imidazolium), 8.66 (br s, ^4J(HH) = 1.8 Hz, 1H, NCHN). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 13.9 (CH_3), 15.4 (CH_3), 46.0 (CH_2CH$_3$), 46.1 (coord. CH_2CH$_3$), 53.5 (CH_2), 54.5 (coord. CH_2), 121.8 (CH imid.), 122.8 (CH imidazolium), 123.2 (CH imidazolium), 123.3 (CH imid.), 129.6 (virtual t, ^{3+5}J(CP) = 10.0 Hz, PPh_3) and one CH arom. masked by this triplet, 130.3 (CH arom.), 130.5 (CH arom.), 130.7 (CH arom.), 132.1 (s, *para*-C PPh_3), 132.2 (virtual t, ^{1+3}J(CP) = 54.4 Hz, *ipso*-C PPh_3), 134.1 (C arom.), 134.3 (virtual t, ^{2+4}J(CP) = 12.2 Hz, *ortho*-C PPh_3), 135.1 (C arom.), 135.6 (NCHN), 174.3 (t, ^2J(CP) = 13.7 Hz, C–Ir), 184.7 (t, ^2J(CP) = 11.7 Hz, CO). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −72.8 (d, ^1J(FP) = 711.3 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −143.1 (sept, ^1J(PF) = 711.3 Hz, PF_6), 21.2 (s, PPh_3). MALDI TOF-MS (CH_3CN, *m*/*z*): 1185.2 [M − PF_6]$^+$. Anal. Calc. for $C_{55}H_{53}F_{12}IrN_4P_4O$ (1330.13): C, 49.66; H, 4.02; N, 4.21. Found: C, 48.99; H, 4.34; N, 4.09%. IR (pure, diamond orbit): 3154 w, 3051 w, 2958 wbr, 1985 s (ν_{CO}), 1564 w, 1480 w, 1435 m, 1350 w, 1260 w, 1220 w, 1154 w, 1095 m, 1027 w, 826 vs, 740 s, 692 vs, 555 sbr, 515 sbr, 499 sh, 455 w, 421 m cm^{-1}.

Synthesis of [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazol-2-ylidene)-bis[(η^4-1,5-cyclooctadiene)iridium(I)chloride], [{IrCl(cod)}$_2$^{Et}(μ-C$_{NHC}$^CH^C$_{NHC}$)] (9)

Compound **2** (0.800 g, 1.90 mmol) in ethanol (15 mL) was rapidly added to a suspension of [Ir(μ-Cl)(cod)]$_2$ (0.639 g, 0.95 mmol) in ethanol (10 mL). The reaction mixture was stirred at room temperature for 15 h and the solvent was removed *in vacuo*. The crude product was dissolved in dichloromethane (15 mL), the solution was filtered and washed with deionised water saturated with KPF_6 (15 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered and addition of Et_2O (50 mL) led to the precipitation of **10** (see below) which was separated by filtration. The solvent was removed *in vacuo* yielding **9** as a light orange solid in 33% yield (0.300 g, 0.31 mmol). Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diisopropyl ether in a saturated acetonitrile solution of the complex. ^{1}H NMR (CD_2Cl_2): δ 1.50 (t, ^3J(HH) = 7.3 Hz, 6H, CH_3), 1.45–1.86 (m, 8H, CH_2 cod), 2.00–2.41 (m, 8H, CH_2 cod), 2.84–2.92 (m, 2H, CH cod), 2.97–3.01 (m, 2H, CH cod), 4.31–4.66 (m, 8H, 2 CH$_3$CH_2 and 4 CH cod), 5.37 and 5.96 (AB spin system, ^2J(HH) = 14.9 Hz, 2H, CH_2), 5.46 and 5.86 (AB spin system, ^2J(HH) = 14.8 Hz, 2H, CH_2), 6.81 (d, ^3J(HH) = 2.0 Hz, 1H, CH imid.), 6.82 (d, ^3J(HH) = 2.0 Hz, 1H, CH imid.), 6.93 (d, ^3J(HH) = 2.0 Hz, 2H, CH imid.), 7.29–7.51 (m, 4H, CH arom.). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.4 (CH_3), 29.3 (CH_2 cod), 29.4 (CH_2 cod), 29.9 (CH_2

cod), 30.0 (CH_2 cod), 33.4 (CH_2 cod), 33.5 (CH_2 cod), 34.0 (CH_2 cod), 34.1 (CH_2 cod), 45.5 (CH_3CH_2), 51.7 (CH cod), 51.8 (CH cod), 52.0 (CH cod), 52.1 (CH cod), 54.1 (CH_2), 84.4 (CH cod), 84.8 (CH cod), 85.0 (CH cod), 120.0 (CH imid.), 120.1 (CH imid.), 120.5 (CH imid.), 120.6 (CH imid.), 128.0 (CH arom.), 128.1 (CH arom.), 128.2 (CH arom.), 128.3 (CH arom.), 129.4 (CH arom.), 129.5 (CH arom.), 137.2 (C arom.), 137.3 (C arom.), 180.1 (C–Ir), 180.2 (C–Ir). MALDI TOF-MS (CH_3CN, *m/z*): 931.2 $[M - Cl]^+$. Anal. Calc. for $C_{34}H_{46}Cl_2Ir_2N_4$ (966.1): C, 42.27; H, 4.80; N, 5.80. Found: C, 42.18; H, 4.69; N, 5.38%. IR (pure, diamond orbit): 3171 w, 3096 w, 2927 m, 2872 m, 2827 m, 1721 w, 1610 w, 1491 w, 1449 m, 1406 s, 1325 m, 1258 s, 1222 s, 1181 m, 1076 m, 1037 m, 996 m, 968 m, 841 s, 802 s, 739 s, 705 vs, 689 vs, 557 w, 521 w, 506 w, 472 w, 433 w, 375 w, 289 s (ν_{Ir-Cl}), 255 m, 141 m, 105 m, 98 m, 78 s, 60 s cm^{-1}.

Synthesis of [(1,3-phenylene)bis(methylene)]-(1-ethyl-imidazolium)-(3-ethyl-imidazol-2-ylidene)-hexafluorophosphate(η^4-1,5-cyclooctadiene)iridium(I)chloride, $[IrCl(cod)^{Et}(CH_{imid.}\text{^}CH\text{^}C_{NHC})](PF_6)$ (10)

Compound **2** (0.800 g, 1.90 mmol) in ethanol (15 mL) was rapidly added to a suspension of $[Ir(\mu\text{-}Cl)(cod)]_2$ (0.639 g, 0.95 mmol) in ethanol (10 mL). The reaction mixture was stirred at room temperature for 15 h and then the solvent was removed *in vacuo*. The crude product was dissolved in dichloromethane (15 mL), the solution was filtered and washed with deionised water saturated with KPF_6 (15 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered and addition of Et_2O (50 mL) led to the precipitation of a solid which was collected by filtration. Two recrystallisations from THF–pentane yielded **10** as an orange solid in 36% yield (0.530 g, 0.68 mmol). ^1H NMR (CD_2Cl_2): δ 1.50 (t, $^3J(HH) = 7.4$ Hz, 3H, coord. CH_3), 1.55 (t, $^3J(HH) = 7.4$ Hz, 3H, CH_3), 1.58–1.88 (m, 4H, CH_2 cod), 2.10–2.37 (m, 4H, CH_2 cod), 2.91–3.00 (m, 1H, CH cod), 3.03–3.11 (m, 1H, CH cod), 4.21 (q, $^3J(HH) = 7.4$ Hz, 2H, CH_3CH_2), 4.35–4.59 (m, 4H, 2 × CH cod and coord. CH_3CH_2), 5.11 (d, $^2J(HH) = 14.9$ Hz, 1H, coord. CH_2), 5.25 and 5.28 (AB spin system, $^2J(HH) = 14.5$ Hz, 2H, CH_2), 6.26 (d, $^2J(HH) = 14.9$ Hz, 1H, coord. CH_2), 6.84 and 6.98 (AB spin system, $^3J(HH) = 2.0$ Hz, 2H, CH imid.), 7.28 (br s, 1H, CH imidazolium), 7.35–7.51 (m, 4H, CH arom.), 7.55 (br s, 1H, CH imidazolium), 8.76 (br s, 1H, NCHN). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.1 (CH_3), 16.4 (coord. CH_3), 29.4, 30.0, 33.4, 33.9 (CH_2 cod), 45.5 (coord. CH_3CH_2), 45.6 (CH_3CH_2), 52.1, 52.6 (CH cod), 53.5 (coord. CH_2), 53.6 (CH_2), 84.7, 84.9 (CH cod), 120.7, 120.8 (CH imid.), 121.8, 122.9 (CH imidazolium), 128.7, 128.9, 129.2, 129.8 (CH arom.), 133.6 (C arom.), 135.5 (NCHN), 138.3 (C arom.), 179.9 (C–Ir). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −72.9 (d, $^1J(FP) = 711.3$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.1 (sept, $^1J(PF) = 711.3$ Hz). MALDI TOF-MS (CH_3CN, *m/z*): 631.2 $[M - PF_6]^+$. Anal. Calc. for $C_{26}H_{35}ClF_6IrN_4P{\cdot}CH_2Cl_2$ (861.15): C, 37.66; H, 4.33; N, 6.51. Found: C, 37.69; H, 4.50; N, 6.73%. IR (pure, diamond orbit): 3160 w, 3097 w, 2961 w, 2923 w, 2873 w, 2823 w, 1563 w, 1449 m, 1408 m, 1350 w, 1328 w, 1260 m, 1225 m, 1154 m, 1095 m, 1024 m, 825 vs, 732 s, 706 s, 555 vs, 377 wbr, 286 mbr (ν_{Ir-Cl}), 104 s, 93 sh, 76 vs, 64 vs cm^{-1}.

Synthesis of [(1,3-phenylene)bis(methylene)]bis(1-ethyl-imidazol-2-ylidene)-bis(η^4-1,5-cyclooctadiene)iridium(I)rhodium(I)dichloride, $[IrRhCl_2(cod)_2^{Et}(\mu\text{-}C_{NHC}\text{^}CH\text{^}C_{NHC})]$ (11)

Solid **10** (0.050 g, 0.06 mmol), $[Rh(\mu\text{-}Cl)(cod)]_2$ (0.016 g, 0.03 mmol) and Cs_2CO_3 (0.026 g, 0.08 mmol) were stirred in acetonitrile (7 mL) at room temperature for 15 h. The suspension was then filtered and the solvent was removed *in vacuo*. The orange solid was dissolved in dichloromethane (15 mL), the solution was filtered and addition of Et_2O (15 mL) led to the precipitation of a solid which was discarded by filtration. The solvent was removed *in vacuo* yielding **11** as an orange solid in 89% yield (0.050 g, 0.05 mmol) as a mixture of two diastereoisomers in a 1 : 1 ratio. ^1H NMR ($CDCl_3$): δ 1.48 (t, $^3J(HH) = 7.7$ Hz, 6H, CH_3), 1.53 (t, $^3J(HH) = 7.7$ Hz, 6H, CH_3), 1.60–1.80 (m, 8H, CH_2 cod), 1.85–2.00 (m, 8H, CH_2 cod), 2.07–2.49 (m, 16H, CH_2 cod), 2.83–2.90 (m, 2H, CH cod), 2.95–3.01 (m, 2H, CH cod), 3.21–3.28 (m, 2H, CH cod), 3.31–3.38 (m, 2H, CH cod), 4.36–4.75 (m, 12H, 4 CH_3CH_2 and 4 CH cod), 5.02 (br s, 4H, CH cod), 5.28 and 6.00 (AB spin system, $^2J(HH) = 14.7$ Hz, 2H, CH_2), 5.43 and 5.86 (AB spin system, $^2J(HH) = 14.8$ Hz, 2H, CH_2), 5.43 and 6.11 (AB spin system, $^2J(HH) = 14.8$ Hz, 2H, CH_2), 5.56 and 5.98 (AB spin system, $^2J(HH) = 14.8$ Hz, 2H, CH_2), 6.70 (d, $^3J(HH) = 2.0$ Hz, 1H, CH imid.), 6.72 (d, $^3J(HH) = 2.0$ Hz, 1H, CH imid.), 6.74 and 6.76 (AB spin system, $^3J(HH) = 2.0$ Hz, 2H, CH imid.), 6.84 (d, $^3J(HH) = 2.0$ Hz, 4H, CH imid.), 7.26–7.45 (m, 8H, CH arom.). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.4 (CH_3), 28.8, 28.9, 29.2, 29.3, 29.4, 29.5, 29.9, 30.0, 32.8, 32.9, 33.3, 33.4, 33.5, 34.0, 34.1 (CH_2 cod), 45.5, 45.8 (CH_3CH_2), 51.7, 51.8, 52.0, 52.1 (CH cod), 54.1, 54.5 (CH_2), 68.1, 68.2, 68.3, 68.4, 68.5 (CH cod), 84.4 (CH cod), 84.8 (d, $J(RhC) = 12.5$ Hz, CH cod), 98.5, 98.6, 98.7, 98.8 (CH cod), 120.0, 120.1, 120.3, 120.4, 120.6, 120.9 (CH imid.), 128.1, 128.2, 128.3, 129.4, 129.6 (CH arom.), 137.3, 137.4 (C arom.), 180.1, 180.2 (C–Ir), 182.3 (d, $^1J(CRh) = 51.1$ Hz, C–Rh), 182.4 (d, $^1J(CRh) = 50.3$ Hz, C–Rh). MALDI TOF-MS (CH_3CN, *m/z*): 841.2 $[M - Cl]^+$. ESI-MS (CH_3CN, 10 V, *m/z*): 841.2 $[M - Cl]^+$. HRMS (ESI) $[M - Cl]^+$: 841.2028 calcd for $C_{34}H_{46}Cl_1IrRhN_4$: 841.2083. Anal. Calc. for $C_{34}H_{46}Cl_2IrRhN_4$ (876.8): C, 46.58; H, 5.29; N, 6.39. Found: C, 42.83; H, 5.59; N, 6.39%. IR (pure, diamond orbit): 3124 w, 3082 w, 2961 w, 2912 w, 2873 w, 2827 w, 1568 w, 1449 w, 1405 m, 1353 w, 1328 w, 1259 s, 1221 s, 1180 m, 1153 m, 1089 s, 1019 s, 956 m, 842 s, 799 vs, 730 s, 698 s, 556 w, 385 m, 285 mbr (ν_{Ir-Cl}), 256 mbr, 142 wbr, 108 w, 98 m, 80 w, 75 m, 66 m, 58 s cm^{-1}.

X-Ray crystal structure determinations of 6 and 9†

The relevant details of the crystals, data collection and structure refinement are given in Table 1. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[61] (graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[62] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms. For complex **9**, absorption correction: MULTI-SCAN,[63] $T_{max} = 0.482$, $T_{min} = 0.410$. Despite this correction, significant residual electron density was found.

The highest peaks (*i.e.*: maximum 3.5 e $Å^{-3}$) are located at less than 1 Å from the metal centres.

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